PATENT ABSTRACTS OF JAPAN

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(71)Applicant : MITSUBISHI CHEMICALS CORP

(72)Inventor : KAWAMATA YUTAKA
TAKAHASHI KUNIMASA

(54) CARBON/GRAPHITE COMPOSITE MOLDING

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a composite molding useful for a separator plate of a solid high polymer type and a phosphate type fuel cell by molding, precisely working and carbonizing a fine particle mixture consisting essentially of a carboneceous carbon compound fine particle having self-sintering property and a graphite carbon fine particle.

SOLUTION: The homogeneously mixed powder is obtained by drying, dehydrating and stirring to mix the fine particle consisting essentially of 10-50 pts.wt. carboneceous carbon compound having self-sintering property at the time of carbonizing and ≥10 μm average particle diameter and 90-50 pts.wt. graphite carbon fine particle having 10-70 μm average particle diameter. An aq. solution containing a particle mutual bonding additive (polyethylene glycol) selected from water soluble compounds having adhesive property is added into the mixed powder and mixed and granulated to form a granulated body having ≤0.5 mm max. particle diameter and molded by a molding machine such as a uniaxial press. The carbon/graphite combined molding is produced by precisely machining the resultant green molding into a high accuracy complicated shape and firing at 1100-1800°C under a non-oxygen atmosphere to carbonize.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to carbon and the black lead composite molding body produced by fabricating the particulate mixture which uses as a main constituent at least one kind of graphite carbon particle chosen from the group which consists of the carbonaceous carbon-compounds particles which have a self-degree of sintering, natural graphite, and an artificial graphite, and carbonizing. Especially this invention provides carbon and the black lead composite molding body which fills the characteristic required of the separator board of solid polymer types, such as bending strength, electrical conductivity, thermal conductivity, gas permeability nature, and corrosion current, and a phosphoric acid type fuel cell. After this invention carries out precision machining of what fabricated with a press the complicated-shaped Plastic solid looked at by the separator board with a slot of a fuel cell, it is only carbonized, and it provides carbon and the black lead composite molding body which can skip a complicated tail end process and with which practical use can be presented.

[0002]

[Description of the Prior Art]Various manufacturing methods of the composite material which consists of carbonaceous carbon and graphite carbon are proposed, and many use at least one kind of carbonaceous carbon powder chosen from organic carbon and carbonaceous carbon, and at least one kind of graphite carbon powder chosen from an artificial graphite and natural graphite. Although there are various compound purposes of carbonaceous carbon and graphite carbon, it is raised that the special feature which black lead generally has with these combination can be endowed with the Plastic solid acquired by calcination of around 1000 **. Filling up the weak point which graphite carbon has with carbonaceous carbon is raised.

[0003]For example, in the example given in JP,59-26907,A. Roll forming (peripheral-speed 0.3 m/min) of the paste which mixed resol system phenol resin 20 weight section with black lead fines 80 weight section which the particle size of 44 micrometers or less beforehand heat-treated at 3000 ** contains 99% at ordinary temperature is carried out, After considering it as the sheet of 4-mm thickness and stiffening this, it heat-treats in maximum temperature of 1000 ** with 1000 **/the heating rate of 10 hours, and is considered as a product. The product characteristics at the time of carrying out after [roll forming] application-of-pressure hardening ($0.1\ kg/cm^2$) are 300-mm x size;400-mmx3.2-mm bulk density [in thickness];1.703 (g/cm^3).

specific resistance; -- 165x10 $^{-5}$ (ohm-cm)

Bending strength;323 (kg/cm^2)

Permeability; 3.5x10 $^{-5}$ (cm^2/sec)

It is indicated that it came out.

[0004]It has put on granting a request function because graphite carbon shares with this gazette the low resistivity of which the compound purpose of organic carbon and graphite carbon is required by the phosphoric acid type fuel cell separator board and the carbide of resol system phenol resin, i.e., glassy carbon, shares low permeability. In this gazette, the forming process by a prevention steel plate is indicated also about the process of a separator board with a slot at the time of a roll with a slot, or hardening with a slot. It is clear that it is not suitable for manufacture of a complicated shape article like [in an organic carbon use system with a large shrinkage amount at the time of carbonization] a separator with a slot like [the combination of a monotonous separator board and a porous electrode board with a slot is common, and] phenol resin in the phosphoric acid type fuel cell of a utilization level in recent years.

[0005]One of this invention persons is him JP,61-199737,A, and Less than quinoline-insoluble;70 % of the weight. Mesophase content; Not less than 40%, heat melting upper temperature limit;400 **, Carbonization yield in 1000 **; by calcinating with the appropriate temperature in an inert atmosphere, after heating preferably the granular material produced by mixing the mesophase containing pitch and graphite powder which have description of at least 70% beyond the heat melting temperature of this pitch and carrying out pressing, The volume change at the time of 1000 ** calcination; the manufacturing method of the graphite Plastic solid which has the characteristic suitable for a separator board called volume resistivity;5.0-m ohm-cm and bending strength;>200 kg/cm^2 is proposed, coefficient of linear contraction having less than 1% of dimensional stability between 3% or less of a raw article and a burned product.

[0006]As a process of the graphite Plastic solid which has the characteristic same with having indicated to JP,61-199737,A in JP,7-35250,B. Blow inactive gas, and the light fraction in the tar distillate containing the mesophase pitch precursor which made graphite fines suspended is heated and distilled off at 350-500 **, The method of using the carbonaceous precursor which deposited the mesophase containing pitch containing 5 to 90 % of the weight of quinolines soluble on the graphite fines surface is indicated.

[0007]The process which makes (1) graphite powder suspended in JP,4-75189,B in the tar distillate containing a mesophase pitch precursor, (2) Heat-treat at 350-500 ** with inactive gas (example: nitrogen gas, carbon dioxide, argon, etc.) to the above-mentioned suspension, The process of the graphite Plastic solid which consists of the process of obtaining the carbonaceous precursor which made the mesophase pitch generating on a graphite-grains child, a process which carries out pressing of the (3) above-mentioned carbonaceous precursor at 400-800 **, and is made into a generation form, and a process of carbonizing or graphitizing the (4) above-mentioned generation form under an inert atmosphere is indicated.

[0008]This process is indicating the method of carrying out hotpress processing as the technique of fabricating a carbonaceous precursor and acquiring a generation form.

[0009]Distortion and residual stress of the carbonization article which a difference with delicate coefficient of linear contraction generated in the process in which the raw article which fabricated carbonaceous precursor

powder in complicated shape like a separator board with a slot is calcinated brings about are cancelable by the hot pressing step which (3) shows. In JP,6-102630,B, (3) processes given [above-mentioned] in JP,4-75189,B are skipped, and the method of carrying out pressing at 800-3000 **, and manufacturing a graphite Plastic solid under a vacuum or an inert gas atmosphere is indicated using a black lead mold etc.

[0010]If this invention is followed, it will become possible to carry out one shot molding of the separator with a slot which has a slot of a large number which intersect perpendicularly with a rear surface. The characteristic simultaneously required of fuel cell separator boards, such as gas impermeability, thermal conductivity, and electrical conductivity, can also be filled. As a method of manufacturing at the process which simplified the graphite Plastic solid excellent in the gas impermeability which can be used as a gas separating plate of a phosphoric acid type fuel cell in JP,62-187167,A, Quinoline insoluble which heat-treated and obtained coal tar, a naphtha-cracking residue, etc. at about 350-550 **; 95 or less % of the weight, Mesophase content; 5-60 weight-section addition of the mesophase containing pitch which is more than [in 1000 **] carbonization yield;70 % of the weight is carried out 35 or less % of the weight to graphite powder 100 weight section chosen from scaly natural graphite or an artificial graphite, Subsequently, this mixture was heated at 700-3000 ** with the heating rate of about 150-3000 **/o'clock under a vacuum or an inert gas atmosphere, and the method of carrying out pressing to the pressure 50 - a 2000 kg/cm^2 grade is proposed. In the manufacturing method of the carbon system composite molding body raw material which consists of one sort or two sorts or more of raw materials chosen from graphite carbon, carbonaceous carbon, an inorganic compound, metal, and metallic compounds in the patent No. 2566589 gazette, and a mesophase containing pitch, (1) The process of making it suspended in the tar distillate containing one sort or two sorts or more of raw materials chosen from graphite carbon, carbonaceous carbon, an inorganic compound, metal, and metallic compounds, and a mesophase pitch precursor, and preparing a slurry, (2) a suspension slurry -- (**) -- the aliphatic series of the carbon numbers 5-20 or alicyclic hydrocarbon, and (**) -- one or more sorts of solvents chosen from the group which comprises the aliphatic series or the alicyclic ketone compound of the carbon numbers 3-5 at a rate of solvent ratio (Sn)2-15 (solvent weight / crude tar weight). [add and] The polycyclic aromatic polymer which contains a mesophase precursor by processing at 0-60 ** in this material surface is deposited, The process of separating the mixture which carries out washing processing of this slurry by which separation post-processing was carried out in the processing solvent at 0-60 ** with a rate of solvent ratio (Sr)1-15 for rinse (solvent weight / crude tar weight), and comprises this raw material and polycyclic aromatic polymer containing a mesophase precursor, (3) The manufacturing method of the carbon system composite molding body raw material using three processes of process ** which heat-treats this mixture at 350-520 ** under an inert gas atmosphere, and makes polycyclic aromatic polymer mesophase-containing-pitch-ize is indicated.

[0011]A mesophase containing pitch can cover perfectly the surface of granular materials, such as SiC, AlN, B_4C, TiC, and Si_3N_4, by this method not to mention graphite carbon or carbonaceous carbon. Therefore, it has the feature which can perform homogeneous pitch covering to two or more constituent content powder surfaces. Although acetone, heptane, etc. are mentioned as a solvent used, it has the feature which can carry out recovery reuse easily. With the size as a metallic mold, carbonize the precision Plastic solid of the complicated shape which mentioned as the example the composite powder which consists of graphite carbon which the mesophase containing pitch prepared by the above-mentioned patent No. 2566589 covered in the

patent No. 2566595, and was not considered conventionally, and to mass production. The granulation method of a carbon system granular material indispensable for offering is indicated.

[0012]This granulation method by the self-degree-of-sintering carbon system granular material and request Graphite carbon, carbonaceous carbon, In the way carry out spray drying of the slurry which made water distribute the carbon system granular material containing at least one kind of granular material chosen from the group which consists of metal and an inorganic compound under existence of a binding material and a wetting agent, and that heated steam is included also corns it in a certain heated air, (1) This binding material does not make foam at the time of carbonization at 1000 **, and remaining coal yield is 10% of the weight or more of an organic compound, and the amount used is 0.01 to 5 weight sections to carbon system granular material 100 weight section, (2) This wetting agent is a non-ion system surface-active agent with which a cloudy point has the clouded sky range of not less than 25 **, and the amount used is characterized by being 0.01 to 3 weight sections to carbon system granular material 100 weight section.

[0013]The granular material with which a granulation is presented can be aimed at all the granular materials obtained by this invention person's above-mentioned precedence invention. A granulation article with a mean particle diameter of 114 micrometers produced by corning the carbon system constituent which covered the scaly graphite surface with the mesophase containing pitch of 97 % of the weight of the amounts of quinolines insoluble by this method A bottom with a thickness of 1.2 mm and length, The light-gage article of the hollow box form which has a partition of a horizontal cross was able to be continuously manufactured with the rotary press machine. The product produced by carbonizing with the heating rate of 9 hours to 1000 ** was finished in the same size as a metallic mold size, and the shrinkage crack of the bottom portion was not accepted, but nearly 100 rates of the yield were obtained. the patent by which the patent No. 2566589 and the patent No. 2566595 were annexed is registered into four nations of U.K. (308824:92.12.23) rice (4985184:91.01.15) ** (P3876913.1;92.12.13) Buddhas (308824:92.12.23).

[0014]When heat-treating and manufacturing the precursor composition of a pitch, or the mixture of the precursor composition of this pitch, and aggregate in JP,6-192660,A, The manufacturing method of the pitch containing composition processed combining the radiation heating technique in a settlement thermal reaction container special under existence of a dispersing agent by request is indicated.

[0015]It can raise epoch-makingly by using the various dispersing agents which were suitable for the raw material in this method in the compatibility of the local hydrophilic material and oleophilic mesophase containing pitch which include many surface activity points like a hydroxyl group or a carboxyl group in the crystal surface looked at by graphite particles, The improvement in fast of the compound characteristic is achieved. Mass production by the commercial scale of homogeneous complex materials was attained by controlling the variation within the large-sized reaction apparatus of the heat treatment temperature which is an important rule factor of composite molding body intensity at **2 ** or less by using radiation heating well.

[0016]

[Problem(s) to be Solved by the Invention]The separator board production technology which filled the characteristic required of the separator board with a slot of the phosphoric acid type fuel cell indicated by the patent which this invention person precedes, A polymer electrolyte fuel cell loading car is brought into the limelight from global environment problems in recent years, and filling the characteristic of the separator board

with a slot which is a member used there can be easily understood from a solid polymer type having operating temperature as low as around 80 ** compared with phosphoric acid type 170-200 **.
[0017]However, since conventional technology is the manufacturing technique which provided the aim in the separator board with a slot of the phosphoric acid type fuel cell as a large-sized power plant, It is necessary to exceed various hurdles for filling the low price demanded with the polymer electrolyte fuel cell as the power plant or the home deferment sized generator of a car, and the huge quantity of production of millions of or more sheets. In the conventional technology which especially this invention person indicated, the cost which manufactures mesophase containing pitch covering black lead composite powder suitable for a fuel cell separator board serves as a big wall. Although mesophase containing pitch covering black lead reveals the desirable characteristic by carrying out a hotpress at 800-900 **, high-volume production capability and a production facility have a technical problem. It is connected with a cost hike in order to make indispensable the spray dryer whose productivity is not so good, although a granulation method suitable for extensive automatic unmanned press forming is also groundbreaking technology.
[0018]On the other hand, the product by the mixture of mesophase containing pitch powder and graphite powder has a problem which should be solved by productivity and a cost aspect in order to make indispensable not less than 300 ** hot press. That is, there is a problem which this invention should solve in making into zero the difference of the cheap product price which a time requires, and the product price which the existing art produces by creation of new art.
[0019]
[Means for Solving the Problem]This invention persons inquired wholeheartedly that new art of making physical properties shown in advanced technology revealing should be created, producing a cheap product. Many requests of the following concerning productivity and a property value which are required of a separator board with a polymer electrolyte fuel cell slot as a major premise of research and development must be filled. Various holes and a slot of a breakthrough which starts gas supply to a sheet surface or rear surface both sides in fuel and an air supply slot which are productivity (b) 200 - 500 mm squares, a performing [mass production of a 1-5-mm-thick board] (**) depth of 1 mm, and 1-2 mm in width, or the side can be installed easily.
Mechanical dimension (**) bending strength, such as property value (**) surface smoothness and curvature, compressive-strength (**) volume resistivity (**) corrosion current (**) gas permeability [0020]This invention persons thought that mass production of cheap products was possible by fulfilling many items about the following raw materials and manufacturing techniques.
An agglomerated powder object (3) whole process with which product (2) automatic unmanned press operation which combined a raw material which is mass-produced and is supplied adequately to a commercial scene can be presented with an efficiency facility appliance from Takao (1) A method of cutting a complicated shape black lead Plastic solid in construction conventional technology, It is obvious to a person skilled in the art that high cost-ization is not avoided in a process of a glassy carbon Plastic solid.
[0021]This invention persons acquire a generation form with a graphite powder object and a self-degree-of-sintering carbonaceous compound granular material which it is mass-produced, and a commercial scene is plentifully supplied, or can be supplied according to a request, A slot was formed in a generation form in this

stage, and a method of manufacturing a solid polymer type and a phosphoric acid type fuel cell separator board by the simple technique of carbonizing this and obtaining a product was indicated to this invention and an invention which applied at the period.

[0022]A method of giving complicated shape to carbon and a black lead composite molding body which this invention persons described above by press one shot molding is considered to be an epoch-making technique. However, many very complicated-to fuel cell separator board-shaped things, art which carries out many [especially] detailed processings to the board side, and products which it is indicated as a patent and cannot be covered only by a method of this invention exist. In carbon industry, the technique of giving various precise shape to a product carbonized or graphitized by post processing is used regularly. Although this may have a problem in a physical-properties side where a self-degree-of-sintering carbonaceous compound used for the usual shaping is unsuitable to processing of a low melting point, low ignition temperature, intensity lacking in machinability, etc., Precision processing shape applied for the characteristic that 10% order linear shrinkage will break out in many cases if a generation form is carbonized rather than anything is distorted, or, It is the common sense of this industry that accuracy required of carbonization and graphitization products in a stage of a generation form for a problem that it is destroyed is not machineable. However, even if it considers performing one-sheet one-sheet micro processing to a product which needs mass production like a separator board of a fuel cell for automobile loading from a problem of work speed of process machinery, a high cost was not avoided but problems -- a large amount of investment is needed also for a production facility -- have accumulated it.

[0023]This invention persons intensity to which carbon and a black lead compound generation form which has the feature from which a size of a generation form and a carbonization Plastic solid becomes small as a metallic mold in coefficient of linear contraction at the time of carbonization are equal to operation of movement on machinery, reversal, etc. enough on a 20-cm square also in the state of a light-gage tabular generation form about 1-3 mm thick. Paying attention to holding, since black lead was a subject's generation form, it also took into consideration having a function enough also in diffusion of heat generated at the time of machining, and what carried out press working of sheet metal of the monotonous generation form was resulted in the way of thinking of a new technique given by machining in precise shape. By finding out that precision with a generation form sufficient at more nearly nearly ten speed of the usual carbonization Plastic solid can be had and processed into a surprising thing by this technique, it doubled that process tolerance of a generation form was held at a carbonization Plastic solid, found out, and this invention was completed.

[0024]In mean particle diameter, a 1-7-micrometer self-degree-of-sintering carbonaceous compound particle and mean particle diameter preferably this invention 10 micrometers or less 10-70 micrometers, Into a mixture which obtained it by dryness preferably by carrying out agitation mixing of the 15-50-micrometer graphite carbon particle. Add solution or water containing at least one kind of additive agent for both particle adhesion chosen from a compound group which has adhesiveness if needed to water solubility, carbonaceous carbon compounds, and graphite carbon of a polyethylene glycol, sucrose, methyl cellulose, a polymer coagulant, etc., and agitation mixing granulation is carried out, A metallic mold is filled up, after a maximum droplet size obtains a granulated body of 0.5 mm or less and dries this, After performing precision processing with process machinery by which normal use is carried out in carbon industry in a plate or a generation form of a near net

shape acquired by fabricating, under an inert atmosphere 1100-1800 **, Let carbon and a black lead composite molding body which has the complicated shape acquired by calcinating at 1200-1600 ** preferably be gists.

[0025]

[Embodiment of the Invention]This invention is explained still in detail below. An embodiment is divided roughly into a raw material, mixing/granulation, shaping, and a calcination system, and is explained.

At least one kind of graphite carbon particle chosen from the group which consists of the shape of a scale, ground-like natural graphite, and an artificial graphite can be used as raw material system (1) graphite carbon particles. An artificial graphite is more preferred by both sides of the physical properties of black lead, and supply stability. For example, KS series by TIMCAL, LTD. can be raised as a desirable artificial graphite. The various artificial graphites supplied from a black lead Plastic solid manufacture can also be chosen as an object.

(2) The particle diameter of graphite particles can be broadly chosen from a viewpoint of a moldability. Even if large not much and small, it stops however, agreeing for the purpose of this invention from a viewpoint with which various-physical-properties values, such as the dimensional stability of volume resistivity, thermal conductivity, Plastic solid intensity, a generation form, and a calcination Plastic solid and gas permeability, are filled simultaneously. 10-70 micrometers of mean particle diameter of graphite particles can be preferably chosen from the range of 15-50 micrometers. If the shape for the slot of a separator board becomes detailed and the demand of dimensional accuracy or gas permeability becomes severe, diameter black lead of a granule will be chosen. The selection which increases the quantity of a self-degree-of-sintering carbonaceous compound from the intensity manifestation mechanism later mentioned the more the more black lead particle diameter becomes small, or makes the mean particle diameter small is made. As typical marketing products which can be used by this invention, there is KS44 of TIMCAL, LTD. in an artificial graphite, and there are CPB and the CPB refined material of a Japanese black lead company with natural graphite.

[0026](3) in order to set up so that the size of a generated type article and carbonization mold goods may become the same, although black lead content can be chosen broadly -- a mixture -- 80 to 65 weight section can be chosen still more preferably 85 to 60 weight section more preferably 90 to 50 weight section. This black lead content range is also a factor governed by sintering physical properties at the time of carbonization of a self-degree-of-sintering carbonaceous compound, and is synthetically determined also based on the self-degree-of-sintering carbon-compounds characteristic. There is room for the black lead origin characteristics, such as electrical conductivity and thermal conductivity, to improve, so that a graphite carbon content is high, although it is natural. However, since graphite carbon swells that sintering properties, mean particle diameter mentioned later, etc. of a self-degree-of-sintering carbonaceous compound are unsuitable at the time of carbonization and it may stop being able to employ the characteristic peculiar to special graphite carbon efficiently, a suitable design is required.

[0027](4) Various self-degree-of-sintering carbonaceous compounds which can be used by this invention are marketed. gamma ingredient (quinoline meltable toluene insoluble element) content can use 5 to 25% of the weight of a self-degree-of-sintering carbonaceous compound preferably three to 30% of the weight as a starting material of carbon and the black lead composite molding body of this invention. If there are too few

gamma quantitative formulas, it is predetermined property value demand-within the limits, and desired intensity cannot be revealed. On the other hand, if too high, it will melt below 100 ** like coal tar, maintenance of Plastic solid shape and maldistribution-ization of a self-degree-of-sintering carbonaceous compound will be caused, and it will not leave for the business of this invention.

[0028]The TGP series by Osaka Kasei Co., Ltd., MPC series, MCMB by Osaka Gas Co., Ltd., KMFC by Kawasaki Steel Corp., KS by the Kureha chemicals company, etc. can be raised as a commercial self-sintering carbonaceous compound which can be used by this invention. It can use, if a high softening point pitch also fills gamma quantitative formula. As long as gamma quantitative formula range which this invention requires is fulfilled, it is satisfactory even if the self-degree-of-sintering carbonaceous compound makes the starting material any of coal tar and petroleum system heavy oil. Even if it is the raw material which enlarged the oxygen content by air oxidation like MPC-1 by Osaka Kasei Co., Ltd., it is satisfactory in any way.

[0029](5) The mean particle diameter of a self-degree-of-sintering carbonaceous compound is an important factor which governs the bending strength, the gas permeability, and the corrosion current value of carbon and a black lead composite molding body in operation of this invention. The particle diameter effect is shown for the goods "TGP3000" marketed from Osaka Kasei Co., Ltd. in an example below. TGP3000 is positioned in the grinding article (a 300-mesh sieve -- vulgar) of the self-degree-of-sintering mesophase containing pitch whose gamma quantitative formula is 21%. A sintered compact can be obtained even if it uses TGP3000 as it is. however, the bending strength of the 1000 ** burned product of the composite molding body mixed and obtained to "artificial-graphite with a [TGP3000 (a 300 mesh sieve -- vulgar) / mean particle diameter] of of 25 micrometers powder =3/7" being below 100 kg/cm^2, and, The bending strength value required of a fuel cell separator board was not able to be filled. The gas permeability of a product and a corrosion current value were also unsuitable fields.

[0030]When jet mill grinding was presented with "TGP3000", the grinding article whose mean particle diameter is 10, 7, and 3 or 1 micrometer was obtained and the Plastic solid was made from the above-mentioned ratio, bending strength 250 kg/cm^2 was obtained in a 3-micrometer article, and gas permeability and corrosion current also decreased in proportion to reduction in particle diameter. The desirable mean particle diameter which can fulfill various physical properties synthetically was 7 micrometers or less. Especially desirable mean particle diameter was 3 micrometers or less. It is possible that this phenomenon originates in self-degree-of-sintering carbon powder being filled up with the particle diameter of self-degree-of-sintering carbon particles becoming small that there is no crevice in a big graphite-grains child's surface.

[0031]Namely, 70% of mean-particle-diameter =25micrometer graphite grains (specific gravity =2.2), mean particle diameter = when 30% of a 50-micrometer self-degree-of-sintering carbon grain (specific gravity =1.8) exists, there is a calculation result that 15 graphite grains exist per self-degree-of-sintering carbon grain. Therefore, it is clear that the existence effect's of the self-degree-of-sintering carbon grain which bears a degree of sintering in the above-mentioned particle diameter relation it is seldom expectable. It becomes the calculation in which 8 and 24 or 303 self-degree-of-sintering carbon grains exist per graphite grains by changing the mean particle diameter of a self-degree-of-sintering carbon grain into 10 and 7 or 3 micrometers. In the case of 10 micrometers, it becomes the calculation with which self-degree-of-sintering carbon covers one third of the one graphite-grains child surfaces. In 7 or 3 micrometers, it becomes the calculation with which

a self-degree-of-sintering carbon grain covers the surface of 1/2 and 1, respectively. It turns out that the desired value of bending strength, corrosion current, and gas permeability is fulfilled by the situation where the calculated value with which a carbon grain covers one half of the graphite-grains child surfaces is acquired from the result of an experiment. In a 3-micrometer article, an effect becomes more perfect.

[0032]It is expected that an electric resistance value will become large on the other hand if the coverage of a carbon ingredient becomes high, and the ohm loss inside a fuel cell becomes large. However, the volume specific resistance values measured by the product "RORESUTA" made from Oil recovery Electron are 1.5 - 1.7-m ohm-cm in mean-particle-diameter the article of 3 micrometers of TGP, and can fill a separator request value. A 1-micrometer article also had the mean particle diameter the same as that of a 3-micrometer article of an effect. Therefore, although the particle diameter of the carbon made from self-sintering which the surface coating takes by change of black lead particle diameter is also changed, it can be predicted by easy calculation.

[0033]Therefore, it can ask for the greatest particle diameter with which the coverage in the above-mentioned calculation can fill about one. If a graphite-grains child grows up, it will seem that the effect that at least not less than 7 micrometers are the same is acquired, but. Since the problem permitted by neither gas permeation nature nor the smooth nature of a slot will occur, and a graphite-grains child's particle diameter itself is restricted, the mean particle diameter of self-degree-of-sintering carbon serves as [if a not much big graphite-grains child is actually used for a part for the slot of a Plastic solid] a maximum with preferred 7 micrometers as a result.

[0034]It is a weight rule factor of a fuel cell system, it is also an important factor which governs the internal exothermic loss of volume resistivity origin, and the thickness of mixing / granulation system separator is so preferred that it is naturally thin. This invention persons examined wholeheartedly the technique of carrying out automatic press shaping of the sheet metal. In order to fabricate with an automatic press, the flow nature of a granular material is a very important rule factor, and in order to usually secure the quick and uniform flow nature in an automatic press metallic mold, an agglomerated powder object is used. The purpose cannot be attained with the simple mixture of graphite powder and carbon powder.

[0035]The spray-drying-granulation method indicated by the patent No. 2566595 gazette which one of this invention persons proposed can supply the black lead / carbon composite powder which was rich in the flow nature which fills the characteristic required of an automatic press. The agglomerated powder object which was rich in the flow nature of desired particle diameter in the slurry solution of the black lead / carbon composite powder which used methyl cellulose and a surface-active agent for the auxiliary agent in accordance with the method of this invention when carrying out spray drying of the steam etc. to the heat source in the air can be manufactured. This invention is included as one form of execution of an invention of the agglomerated powder object manufacturing method by the method of the patent No. 2566595 gazette indication. This invention persons examined the method of mixing and a granulation further.

[0036](6) In this invention, when the success or failure of operation which mix uniformly a 10-70-micrometer graphite-grains child with a 1-10-micrometer detailed self-degree-of-sintering carbonaceous compound cover the graphite-grains child surface with a self-degree-of-sintering carbon particle and make a Plastic solid reveal the necessary characteristic, it becomes very important. Remarkable difficulty is accompanied by

homogeneous mixing of this detailed particle. Namely, if the mixed device accompanied by compression like a grinding machine is used, it is remarkable in the graphite-grains child who has scale-like structure and reveals a self-moldability by compression, and the natural graphite which has a huge scale especially, but. Before mixing with self-degree-of-sintering carbonaceous compound particles, a graphite carbon particle adheres mutually and a desired characteristic manifestation becomes impossible. In the mixer to which a grinding function like a ball mill gives priority on the other hand, the manifestation of the Plastic solid performance which the raw material itself was ground and was designed with the predetermined mixture ratio becomes difficult.
[0037]In the stirring mixer machine represented by the high speed mixer, in order to mix a granular material in the state of free floating using a moving vane, the above problems do not arise easily. This invention persons searched for mixing requirements by the high speed mixer (made by FUKAE POWTEC CORP.). As a result, carbon powder and graphite powder Not less than 50 **, It found out that the very good mixed state could attain in several minutes by mainly performing mixing using an agitator, purging with dry air or nitrogen gas so that humidity may not enter in a mixing chamber from a room temperature in a 100 ** temperature requirement, after drying at around 100 ** preferably.
[0038](7) After corning this mixed powder by the same machine, the granulated body from which moisture was removed by desiccation has the particle diameter of 0.5 mm or less. The spherical particle which specifically passes a mesh <0.425mm screen about 100% was obtained. It was found out that a desired detailed spherical particle can be manufactured with sufficient reproducibility by presenting rotation more nearly high-speed than common sense with an agitator conventionally also in this case. Therefore it is made simple at these new discovery, and came to see completion of high mixing and granulation method of productivity.
(8) A granulation is attained by adding granulation liquid in the state of stirring to the granular material which mixing ended. Granulation liquid can choose various gestalten. But simple granulation liquid is water. However, the granulated body which is obtained after desiccation in the case of a water granulation collapses easily. Therefore, although it is unsuitable for a manufacture gestalt which conveys an agglomerated powder object by big container, the function of a request of a water granulation is obtained at the factory where a granulation, desiccation, and shaping are systematized. A granulated body with higher intensity can be obtained by adding in water by using as a caking auxiliary agent the various compounds which combine water solubility, such as a polymer coagulant, a polyethylene glycol, methyl cellulose, and sucrose, and a coking property.
[0039]The purpose is attained by choosing the caking auxiliary agent which does not contain an element which produces corrosion and generation of heat by remaining in a separator and participating in electrochemical reaction. If the intensity of the granulated body obtained here is too high, even if it will fabricate by a press molding process with specified pressure, a grain stops however, collapsing. When extreme, a Plastic solid section is observed as combination of granulation particles. In such a case, the request physical properties represented by gas permeability are no longer fulfilled.
[0040]Therefore, it is necessary to optimize the addition of a caking auxiliary agent according to each physical properties. Specifically by methyl cellulose, a polymer coagulant, or a polyethylene-glycol system, it is chosen 0.1 to 0.5% of preferably 0.05 to 1.0% at the outside rate regardless of a degree of polymerization. In sucrose, it is preferably chosen 1 to 3% of more preferably 0.5 to 5% 0.1 to 10% at the outside rate. It originates in

sucrose forming the film containing a countless crack to the difference of an addition forming a firm film by dryness in a polyethylene glycol.

[0041]That is, in a polyethylene glycol, since a firm film works in the direction which prevents a grained collapse at the time of press pressurization, it is required to lessen the addition as much as possible. On the other hand, since the grain cannot collapse easily at the time of the usual handling if a polyethylene glycol is added, the extremely stable flow nature is secured. This granulated body can respond to the general material uniform filling-up method in an automatic press enough. The same effect is expectable also by sucrose or methyl cellulose. By these systems, the part remains in a Plastic solid as carbon at the time of carbonization, and since it acts as a binder of a carbon grain and graphite grains, it contributes to improvement in Plastic solid intensity. It contributes also to improvement in the density of a carbonization article.

[0042](9) It is preferred to perform mixing and a granulation independently in a commercial scale. By this, complicated processes, such as mixing chamber desiccation, affix removal, etc. at the time of introducing a dried powder object into the apparatus using water, can be skipped, and mixing and granulation each process can be mostly operated by uninhabited. Press forming is presented with it after a granulation article passes through a drying process. Include [moisture], it can fabricate, but it is obvious to a person skilled in the art that it is a gestalt unsuitable for automatic shaping. A magnetron dryer can be given to apparatus like a high speed mixer, and a granulation article can be dried. In this case, since moisture evaporates from an inside, it can form a countless stoma in an agglomerated powder inside-of-the-body part, by molding pressurization, promotes a grained collapse further and contributes to improvement in the gas opacity of a Plastic solid.

[0043]A shaping system fuel cell separator board has many which form complicated-shaped fuel gas (hydrogen) and the channel of an oxidizer (air) in the surface. The information disclosed by the patent to the shape is various. Many proposals are made by manufacturers, such as what formed the channel only in one side, and a thing formed in both sides. Although it is obvious in the person treating a carbon molding material, it cannot but become a product expensive as a result which occupies a machine tool very difficultly for a long time to form the applied complicated shape on the board carbonized or graphitized. Furthermore, in a high hardness raw material, mass production is very difficult like glassy carbon. The purpose of this invention forms the applied complicated shape with the machine tool machine generally used for the generation form after [monotonous] press forming is carried out in carbon industry. An end mill, an engine lathe, etc. can be used as a machine tool. Cutting can be performed by being oilless. There is the feature of this invention in holding accuracy sufficient at the speed of 5 times or more with the end mill cutting tool of the two-sheet edge used for processing of carbonization products, and processing being possible. In the process machinery furnished with the saw-like cutting tool which has many edges, the cutting speed can take ten to 20 times. Since a product configuration does not change by generation of heat etc. even if many saw-like tools are put in order and it cuts a slot at a stretch, it is a merit of this invention that the cutting speed in a commercial scale can be set as a several 10 times as many level as a carbonization article.

[0044]Since ultra-precision machining of a lot of separator boards will be easily made with a small number of cutting machine if the technique of this invention is followed, the cost cut effect becomes very large. Since a hole, a slot, etc. on the side can be formed easily, the same effect as press one shot molding is expectable. the success or failure of this invention -- the size of a generation form and a carbonization Plastic solid --

parenchyma -- it is started whether it becomes the same. It was examined whether the difference in dimension of the generation form which requires for the example of representation beta quantitative formula of coal tar origin called TGP3000 in combination with black lead in the self-degree-of-sintering carbonaceous compound around 21%, and a carbonization Plastic solid could obtain the composite powder for Plastic solids of real zero.

[0045]TGP3000 is a raw material which generates a cracked gas ingredient in large quantities at 200-400 **, and has physical properties unique as a mesophase containing pitch. However, the TGP independent Plastic solid has the characteristic which becomes high intensity extremely. TGP3000 ground to the various particle sizes described previously is variously corned at 2% of the rate outside after-mixing sucrose with a ratio with the artificial graphite by TIMCAL, LTD. "KS44" by a high speed mixer, The dry granular material was fabricated by moulding pressure ^{2} of 1 t/cm, temperature up was carried out to 1200 ** with bottom 1 ** the heating rate for /of an inert gas atmosphere, the carbonization Plastic solid was acquired, and the dimensional change before and behind calcination was observed.

[0046]As a result, in the mean-particle-diameter article of 3 micrometers of TGP3000, it was before and after calcination in 3000= 30% of TGP, and 44= 70% of KS, and coefficient of linear contraction was real zero. Coefficient of linear contraction was less than 1% also within the limits of 3000= 27 to 30% of TGP. Although optimum value [the] was somewhat changed by change of the mean particle diameter of TGP3000, the presentation of coefficient-of-linear-contraction real zero has been set up within the limits of 3000= 26 to 30% of TGP. It is guaranteed that carry out precision processing of the complicated shape to a generation form, and the workability is inherited by the product by presentation setting out of coefficient-of-linear-contraction zero having been checked. TGP2000 (a 200-mesh sieve -- vulgar) marketed did the same examination, and acquired results similarly. That is, it found out that a constituent called TGP had agreed for the purpose of this invention.

[0047]This invention persons did the same examination using "KMFC" and "MCMB" which are the self-degree-of-sintering carbon materials marketed with dry blending which is a component of this invention, and the dry agglomerated powder object prepared through the process of wet agglomeration, and found out the presentation of coefficient-of-linear-contraction zero like TGP3000.

[0048]In calcination system this invention, a product can be obtained by a self-degree-of-sintering carbonaceous compound heat-treating under an inert atmosphere to the temperature which becomes carbonaceous carbon. A self-degree-of-sintering carbonaceous compound emitting hydrogen at around 900 **, and completing carbonization is generally known. Therefore, carbonization will be completed if it heat-treats to 1000 ** known as a usual carbonization temperature. However, 1100-1800 ** of carbonization temperature [1150-1600 ** of] in this invention is preferably chosen from 1200-1500 ** still more preferably. The reason for choosing a temperature higher than the conventional carbonization temperature is in reduction of corrosion current.

[0049]namely, -- a proton type fuel cell -- phosphoric acid -- be -- the solid polymer type polymers in which the sulfuric acid group was fixed to the poly membrane -- be, since current flows into the separator board of an operating state and moisture and a proton live together, The electrochemical reaction in the functional group to which the amount which the difference of operating temperature brings about exists in the end face of that,

graphite crystals, or a carbon crystal occurs, and it is observed as corrosion current. When extreme [the crystalline structure of black lead or carbon is destroyed by corrosion current, and], the phenomenon in which a separator board becomes tattering occurs. As for especially the graphite-crystals end face having many functional groups, a ****** cage and here become a source of release of corrosion current well. A corrosion current reaction occurs by the functional group which remains when carbonaceous carbon also has insufficient carbonization.

[0050]Three kinds can be raised as a measure against corrosion current of this invention. First, about the reaction inhibition of a graphite-crystals end face functional group, self-degree-of-sintering carbonaceous compound particles cover the black lead end face at the time of mixing/granulation, at the time of carbonization, by melting sintering of self-degree-of-sintering carbonaceous compound particles, the graphite-crystals end face is protected and the reactivity is reduced. To the field exposed by cutting, next, phenol system resin, methyl cellulose, It dries, after spraying the solution of at least one kind of compound chosen from sucrose. After forming this compound thin film in the field exposed by cutting, a desirable effect is acquired by deterring forming a glassy carbon-like thin film by presenting carbonization, and contacting the exposure graphite-crystals end face and the carbonaceous crystal end face of a steam or a proton. Next, it is in suppressing accelerating advance of the electrochemical reaction which occurs when the functional group of a carbonaceous carbon crystal and a graphite carbon crystal is removed beforehand and a lot of functional groups remain by setting carbonization temperature as a mentioned range, and securing prolonged stability. If 1200-1500 ** of desirable temperature requirements are chosen especially, an initial corrosion current value will decrease sharply or less [at the time of 1000 ** calcination] to 1/10, and will change with the current value in tolerance level also by prolonged operation.

[0051]As for this, since BN used at the time of shaping as a cause which, on the other hand, raises an initial corrosion current value is raised, it is preferred not to use it or to reduce the amount used as much as possible. Changing to carbonaceous carbon is known well, emitting cracked gas in the carbonization temperature region which is 200-500 ** about, although a self-degree-of-sintering carbonaceous compound differs in the range a little with the starting material, a heat treating method, and gamma quantitative formula. At 200-500 **, if there are too many gas yields per unit time from a Plastic solid, swelling of a Plastic solid will occur with gas pressure, and it not only worsens various physical properties, such as bending strength, gas permeability, and electrical conductivity, but the gestalt of a product will sometimes be lost.

[0052]A heating rate is made to optimize with the content in the mixture for Plastic solids of a self-degree-of-sintering carbonaceous compound, gamma quantitative formula, and the area and moulding pressure of a Plastic solid. Although these techniques are technical ranges publicly known to a person skilled in the art, it is requested that a 150-600 ** carbonization temperature requirement should also set the heating rate of the generation form of this invention as 0.2-2 ** the range for /by 0.01-5 **/more preferably [it is desirable and] than a part for 0.1-3 **/. If oxygen contacts a Plastic solid from the exterior at the time of calcination, in a 200-500 ** temperature region, a self-degree-of-sintering carbonaceous compound will absorb oxygen, and will deteriorate in an oxygen content carbonaceous compound. In this case, since distortion and destruction of a product will be brought about in order that a difference may appear in coefficient of linear contraction between the compounds which did not receive oxidation at the time of carbonization, it is necessary in this temperature

region during calcination to deter invasion of oxygen.

[0053]Although it is the art known from the former as an oxygen invasion deterring method in this temperature region, carbonization under inactive gas (nitrogen gas is preferred) atmosphere is raised. Since the "corks breeze" which is carbonization packing usually used does not have the oxygen invasion deterrence capability in this temperature region, The method of installing the oxygen penetration deterrence layer from which this invention persons mixed and got the linseed oil to the corks breeze indicated by JP,5-186265,A in the container upper part, and making real zero oxygen invasion to a 500 ** field can also be used. The same effect is acquired also by the method of mixing the suitable grinding article of TGP with a corks breeze instead of the linseed oil. Carbonization of not less than 600 ** can be arbitrarily chosen from 1 ** - 10 ** the range for /. Although desorption of hydrogen in a carbonization culmination occurs here, it is desorption in the stage which improved already in intensity, and since the gas passageway is also secured, slow speed temperature up is not required.

[0054]An example is given and the contents of this invention are explained below to an example still more concretely.

75 g of self-degree-of-sintering carbonaceous compound particles (a jet mill grinds TGP3000 by Osaka Kasei Co., Ltd.) whose mean particle diameter which reached the dry constant mass with the hot wind cyclical form dryer held at 1110 ** of examples is 3 micrometers are supplied to the high speed mixer by FUKAE POWTEC CORP. (LFS-GS-2J type), Dry nitrogen was blown off from the agitator and the chopper shaft, 175 g of artificial graphites by TIMCAL, LTD. (KS44) whose mean particle diameter is 25 micrometers were thrown in in 5 minutes with the spatula, stirring at the agitator number of rotations of 500 rpm, and the chopper number of rotations of an average of 1000 rpm, and also stirring was continued for 5 minutes. When observed from the inspection hole of the lid, the granular material was mixed smoothly.

[0055]The granulation service-water solution which consists of the sucrose 5g and the water 75g was poured into the above-mentioned mixture under mixing in 2 minutes at the agitator number of rotations of 2000 rpm, and the chopper number of rotations of 500 rpm, and the granulation was continued for 3 minutes. The obtained granulated body was dried with a 105 ** hot wind cyclical form dryer, and it cooled to the room temperature. The plus sieve was separated by the screen of 0.425 mm of meshes of a net. Not less than 99% was collected as a minus sieve. The 200.0 mm long and 200.0 mm wide metallic mold was installed in 600 t of biaxial type pressing machine, and using the vertical section force piston which has a smooth side, the minus sieve granulated body 216g was thrown in, it fabricated with the moulding pressure of 1-t [/cm] ^{2} after degassing operation, and the 3.3-mm-thick monotonous generation form was acquired. End mill processing was presented with this generation form. The drill with a diameter of 1 mm of a two-sheet edge was operated by a part for 2500-rpm and travel-speed/of 320 mm, it left both ends 30 mm, and a slot a depth of 1 mm and 1 mm in width was minced to both sides with the flute width of 2 mm. The slot adopted the form which intersects perpendicularly by a rear surface.

[0056]The Plastic solid upper and lower sides were inserted with the black lead board with a thickness of 50 mm which has the smooth side installed in the stainless steel container, the circumference was covered by the corks breeze, and the upper part installed the antioxidant layer which mixed the linseed oil with the corks breeze. Furnace cooling was carried out, after heating to 1200 ** with the heating rate of 1 **/m and

maintaining at 1200 ** for 2 hours, supplying nitrogen with the speed of supply for 5L/from the alumina pipe which installed the container in the muffle furnace and was introduced into the breeze layer from the upper part of the lid. The acquired carbonization Plastic solid gave coefficient of linear contraction of 0.4% compared with the metallic mold size. The slot formed with the end mill was carbonized as it was, it was distorted, and a bend and partial destruction were not accepted. A specimen 100 mm in length and 10 mm in width was cut down by cutting from the flat part, the three point bending examination was done, and 2.5 kgf/mm bending strength ^{2} was obtained.

[0057]The specimen of 25 mm squares was cut down from the flat part, it asked for gas permeability by back pressure 1 kg/cm^{2} using nitrogen, and /cm^{2} was obtained by 3x10 $^{-5}$Ncc/. Volume resistivity was measured for this specimen using RORESUTA made from an oil recovery electron, and 1.6-m ohm-cm was obtained. The specimen (10 mm x 10 mm) was cut down from the flat part, corrosion current was measured, and 80microA/cm^{2} was obtained 1000 minutes afterward.

[0058]

[Effect of the Invention]This invention makes it possible to provide cheaply complicated-shaped carbon and the black lead composite molding body which fulfills the various characteristics required of the separator board of solid polymer types, such as bending strength, electrical conductivity, thermal conductivity, gas permeation nature, and corrosion current, and a phosphoric acid type fuel cell.

[Translation done.]